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345,553

From: Geist, Gary
Sent: Wednesday, May 09, 2001 10:54 AM
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I would like a copy of the following references for 09/700,494:

1. Henne et al, Am. Chem. Soc. vol. 67, pp 918 and 919. 1945

2. Bulletins de L'Academie Royale de Belgique - Class de Sciences (1902) p. 757.

These are references printed on issued patent US 2,559,629. Thank you. Please deliver to CM1-8B19.

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0002-7863

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Summary

The action, at low temperatures, of anhydrous aluminum bromide promoted by hydrogen bromide upon the branched chain hexanes has been studied.

1. 2-Methylpentane and 3-methylpentane were isomerized with only traces of cracking yielding what was apparently an equilibrium mixture of the two.

2. Unlike its isomers, 2,2-dimethylbutane was not appreciably isomerized.

3. The formation of 2,2-dimethylbutane from the other hexanes has been correlated with cracking.

4. 2,2-Dimethylpropane and normal paraffin hydrocarbons were absent in all reaction products identified.

CLEVELAND, OHIO

RECEIVED MAY 29, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Preparation of Polyfluorinated Acids*

BY ALBERT L. HENNE, THOMAS ALDERSON AND MELVIN S. NEWMAN

Fluorinated acids have been made by halogen substitution, but in poor yield due to extensive decomposition.¹ They have also been made by oxidation of fluorinated alcohols,² a procedure which is defeated by the difficulty of obtaining these alcohols. For trifluoroacetic acid, there is a practical preparation which consists in a lengthy heating of *m*-trifluorotoluidine with chromic acid, for a yield of 55 to 60%.³ With trifluorotoluene now available commercially, this preparation could be made economically; it is, however, an individual case.

The method proposed here is the oxidation with alkaline permanganate of a judiciously fluorinated olefin. This method is made possible by the resistance of sufficiently fluorinated acids toward the haloform reaction. The oxidation is fast and almost quantitative. The limiting factors are that the fluorine atoms should be sufficient in number and should be properly placed. The method with its limitations is illustrated by the preparation of $\text{CF}_3\text{CO}_2\text{H}$ from $\text{CF}_3\text{CCl}=\text{CCl}_2$, $\text{CHF}_2\text{CO}_2\text{H}$ from $\text{CHF}_2\text{CH}=\text{CCl}_2$ and $\text{CF}_2\text{ClCO}_2\text{H}$ from $\text{CF}_2\text{Cl}-\text{CCl}=\text{CCl}_2$ and by the failure to obtain $\text{CFCl}_2-\text{CO}_2\text{H}$ from $\text{CFCl}_2\text{CCl}=\text{CCl}_2$. Its extension to the preparation of a number of acids with a CF_2 group in alpha position, and to ketones with a CF_2R or a $-\text{CF}_3$ group in alpha position is now under investigation. This method has been applied to preparations on a larger scale without further difficulties.

Experimental Details

Trifluoroacetic acid was prepared by oxidation of $\text{CF}_3\text{CCl}=\text{CCl}_2$,⁴ in accordance with the equation: $3\text{CF}_3\text{CCl}=\text{CCl}_2 + 4\text{KMnO}_4 + 14\text{KOH} \rightarrow 3\text{CF}_3\text{CO}_2\text{K} + 4\text{MnO}_2 + 9\text{KCl} + 3\text{K}_2\text{CO}_3 + 7\text{H}_2\text{O}$. The apparatus consisted of a five-liter, three-neck flask fitted with an efficient reflux

* This manuscript, after acceptance for publication, was referred to the National Defense Research Committee, and at their request was withheld from publication until clearance was granted on May 5, 1945.

(1) Swarts, *Mém. Couronnés Acad. Roy. Belg.*, 51 (1896); 54 (1896); *Bull. Acad. Roy. Belg.*, [3] 31, 675 (1896).

(2) Swarts, *Bull. classe sci., Acad. Roy. Belg.*, 757 (1902).

(3) Swarts, *ibid.*, 343-370 (1922).

(4) Prepared as shown in *THIS JOURNAL*, 63, 3478 (1941); 64, 1157 (1942).

condenser, a sealed stirrer and a two-hole stopper bearing a thermometer dipping into the liquid and a separatory funnel. In the flask were placed 230 g. (calcd. 210 g.) of potassium permanganate, 260 g. (no excess)⁵ of potassium hydroxide and 3 liters of water. The mixture was heated with continuous stirring to a temperature of 65-70°, which was then maintained throughout the oxidation. One mole (199 g.) of $\text{CF}_3\text{CCl}=\text{CCl}_2$ was added progressively, as fast as the refluxing caused by the reaction would permit. The completion of the oxidation was detected by the disappearance of two-phase droplets in the reflux, usually after six to eight hours. At this stage a one-hour heating period at 100° may be resorted to, but is superfluous when the reaction has been conducted swiftly, with efficient stirring.

After cooling to 40°, the dropping funnel was replaced by an inlet tube reaching into the liquid, and a rapid stream of sulfur dioxide was passed until the purple color just disappeared. Sulfuric acid of 50% concentration was added through the reflux condenser until the carbon dioxide evolution ceased. The addition of sulfur dioxide was then resumed until the manganese dioxide just disappeared. This operation lasted about thirty minutes and required cooling to maintain the temperature below 60°; it should not be interrupted, lest the manganese dioxide should settle in a cake. The pink solution was neutralized until a permanent precipitate of manganese hydroxide just appeared, and then boiled down in the absence of air until crystals began to separate. After rapid cooling, one mole of 50% sulfuric acid was added; the crystals were allowed to settle and the supernatant liquid was decanted while cool. From the solution, trifluoroacetic acid was ether-extracted; with the ordinary glass devices for continuous extraction this took about thirty hours. Fractional distillation of the ether extract gave first ether which was used again in a subsequent operation, then a fraction boiling about 101° which was a mixture of 80% of trifluoroacetic acid with 20% of water. To isolate the pure acid, the sodium salt was formed by neutralization with a 20% solution of sodium carbonate, evaporation to dryness, extraction with absolute ethanol, and evaporation of the alcohol to leave anhydrous trifluoroacetate. A treatment of the salt with concentrated sulfuric acid yielded anhydrous trifluoroacetic acid. The net yield was 90%.

It is possible to avoid both the sulfur dioxide treatment and the ether extraction. After completion of the oxidation, the mixture is cooled, acidified with 50% sulfuric acid. The manganese dioxide is filtered off and extracted three times with 300-ml. portions of 25% sulfuric acid. The filtration and extraction are frequently inconvenient and this is the reason why the other procedure was preferred. The filtrate and washing are distilled until the

(5) As much as 20% excess of caustic can be used but is not recommended. Larger excess, particularly in the case of higher concentrations, cause the formations of increasing amounts of fluoroform...

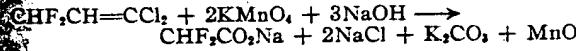
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temperature of the vapors reaches 115°. The distillate is neutralized with 20% sodium carbonate and evaporated to dryness then extracted with absolute alcohol as indicated above. The net yield is 84%.

Esterification proceeds normally in the presence of sulfuric acid. It is entirely superfluous to use anhydrous trifluoroacetic acid as either the 80% solution, or the unrefined sodium salt can be used. The esterification is fast and complete. The operation is best carried out by heating the reagents in a flask fitted with a distilling column. A mixture of ether, ethanol and ester distills at 54-55°, which separates into two layers at about room temperature. From this mixture, the alcohol is removed by repeated washings with a cold concentrated solution of calcium chloride, followed by vigorous agitation with solid calcium chloride and drying over phosphorus pentoxide. The esterification is quantitative, but the yield of pure ester depends markedly on the skill of the operator.

The physical constants listed by Swarts⁴ for the acid and the ethyl ester were duplicated.

Trifluoroacetic acid was prepared in accordance with the equation



The equipment was that used for the preparation of trifluoroacetic acid. The oxidation was however more exothermic, which led to alterations in the mode of operation. To a stirred solution of 670 g. of potassium permanganate (calcd. 632 g.) and 250 g. of sodium hydroxide (calcd. 240 g.) in three liters of water, 295 g. (2 moles) of $\text{CHF}_2\text{CH}=\text{CCl}_2$ ⁶ were added through a dropping funnel. This addition brought the temperature of the liquid rapidly from 28 to 70° where it was held by external cool-

(6) This olefin was first made by A. M. Whaley (Research Chemicals, San José, California) by condensing $\text{CHCl}=\text{CHCl}$ and CHCl_3 on AlCl_3 to $\text{CHCl}_2=\text{CHClCHCl}_2$, removing HCl to obtain $\text{CHCl}_2\text{CH}=\text{CCl}_2$ and fluorinating to $\text{CHF}_2\text{CH}=\text{CCl}_2$ in the manner previously described.⁴

ing while the addition was continued as fast as practicable. The oxidation was virtually complete in three hours. This was verified by heating to 85° and observing that the reflux was free of organic layer. After cooling the working up of the reaction products followed the preceding procedure. The trifluoroacetic acid was finally obtained in a 90% mixture with water, which boiled between 125 and 133° as a clear colorless sharp smelling liquid which fumed slightly in the air. The purification to the absolute acid was done via the sodium salt. The net yield was 86%.

The compound is adequately described by Swarts.³ Its esterification does not require the use of pure acid. Both the crude or the sodium salt have been quantitatively transformed into various esters, the purification of which is mostly a matter of removing entrained alcohol.

Trifluorochloroacetic acid was prepared from $\text{CClF}_2\text{CCl}=\text{CCl}_2$,⁴ in accordance with the equation $3\text{CClF}_2\text{CCl}=\text{CCl}_2 + 4\text{KMnO}_4 + 14\text{NaOH} \rightarrow 3\text{CF}_2\text{CICO}_2\text{Na} + 4\text{KCl} + 5\text{NaCl} + 3\text{Na}_2\text{CO}_3 + 4\text{MnO}_2 + 7\text{H}_2\text{O}$. The apparatus and procedure were substantially those for trifluoroacetic acid, except that an excess of caustic always was avoided. The oxidation was slower, and would not maintain itself, so heat was supplied throughout the operation. After two days, the oxidation was interrupted, despite the fact that it was not yet complete. The material was worked up as indicated above, finally to obtain 47 g. of acid, at the expense of 108 g. of $\text{CClF}_2\text{CCl}=\text{CCl}_2$. This is a 70% yield. The acid is described by Swarts.

Summary

For the preparation in high yield of fluorinated acids a method is presented which consists in the alkaline oxidation of an adequately chosen fluorinated olefin. This method is made possible by the resistance of fluorinated acids to the haloform reaction.

COLUMBUS, OHIO

RECEIVED NOVEMBER 3, 1943

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Polarographic Behavior of Chloro and Bromo Complexes of Stannic Tin

BY JAMES J. LINGANE

Since the standard potential of the stannic ion-stannous ion couple is about -0.10 v. *vs.* the saturated calomel electrode one might infer that stannic ion should be easily reducible at the dropping electrode, but actually this is not true. With solutions of stannic tin in 1 to 2 M perchloric acid no indication of a reduction wave is obtained before the discharge of hydrogen. In such solutions the predominating ionic species is probably the hexaquostannic ion $\text{Sn}(\text{H}_2\text{O})_6^{+4}$, and apparently the rate of reduction of this ion is so slow that no appreciable reduction occurs during the short life of each mercury drop.

Furthermore, no indication of a reduction wave is observed with stannic tin in sodium hydroxide solution, nor from acidic, neutral, or basic tartrate solutions, nor from acidic oxalate solutions.¹ Apparently the complexes present in these solutions are either too stable, or are reduced too slowly, to permit the occurrence of a wave.

In previous studies it was observed that a

rather poorly developed wave is obtained from solutions of stannic tin in 1 N perchloric acid containing 0.5 N sodium chloride,² or from 1 N hydrochloric acid.¹ Since the determination of tin from the stannic state is obviously much more convenient than its determination from the stannous state, and since satisfactory conditions for the polarographic determination of stannic tin have not heretofore been described, it seemed worth while to investigate more thoroughly the wave obtained from chloride media. It has been found that when the concentration of chloride ion in the supporting electrolyte is made very large (greater than 4 M), so that the *aguo* stannic ion is converted more or less completely into the *chloro* complex, SnCl_6^{4-} , a very well developed doublet wave is obtained which is entirely suitable for analytical purposes. A fairly well developed doublet wave is also obtained from the reduction of the hexabromostannate ion in concentrated bromide solutions.

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

(1) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, 15, 583 (1943).

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